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Large Second-Harmonic Response of C_{60} Thin Films

by

X.K. Wang, T.G. Zhang, W.P. Lin, S. Liu, G.K. Wong,
M.M. Kappes, R.P.H. Chang, and J.B. Ketterson

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X.K. Wang, T.G. Zhang, W.P. Lin, S. Liu, G.K. Wong, M.M. Kappes, R.P.H. Chang, and J.B. Ketterson

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Second harmonic generation measurements were performed using 1.064 μm pulses provided by a Nd:YAG laser. A bulk second-order susceptibility $\chi^{(2)}_{zzz} = 2.1 \times 10^{-9}$ esu was observed at room temperature, which is about 1.5 times the $\chi^{(2)}$ value of quartz. $\chi^{(2)}$ values in a poling field were studied as a function of temperature; the largest value occurred at a nominal temperature of 140°C where $\chi^{(2)}$ is ten times larger than the room temperature value.

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Large second-harmonic response of C_{60} thin films

X. K. Wang
Department of Materials Science and Engineering, Materials Research Center, Northwestern University, Evanston, Illinois 60208

T. G. Zhang and W. P. Lin
Department of Physics and Astronomy, Materials Research Center, Northwestern University, Evanston, Illinois 60208

Sheng Zhong Liu
Department of Chemistry, Northwestern University, Evanston, Illinois 60208

G. K. Wong
Department of Physics and Astronomy, Materials Research Center, Northwestern University, Evanston, Illinois 60208

Manfred M. Kappes
Department of Chemistry, Northwestern University, Evanston, Illinois 60208

R. P. H. Chang
Department of Materials Science and Engineering, Materials Research Center, Northwestern University, Evanston, Illinois 60208

J. B. Ketterson
Department of Physics and Astronomy, Materials Research Center, Northwestern University, Evanston, Illinois 60208

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Second harmonic generation measurements were performed using 1.064 μm pulses provided by a Nd:YAG laser. A bulk second-order susceptibility $\chi^{(2)}_{zzz} = 2.1 \times 10^{-9}$ esu was observed at room temperature, which is about 1.5 times the $\chi^{(2)}$ value of quartz. $\chi^{(2)}$ values in a poling field were studied as a function of temperature; the largest value occurred at a nominal temperature of 140 °C where $\chi^{(2)}$ is ten times larger than the room temperature value.

There is currently much interest in nonlinear-optical materials based upon conjugated-carbon-polymers characterized by extensive π-electron-delocalization, due to their intrinsically large nonlinearities, rapid response times, and high threshold damage levels.[1,2] Progress, however, has been modest in spite of the global effort.

Buckminsterfullerene (C_{60}) is a hollow cage, all carbon molecule with 60 carbon atoms connected by a conjugated backbone incorporating twelve pentagons and twenty hexagons. When measured along the diameter it has a mean atom-to-atom distance of 7.065 Å.[3] Based on its π-electron delocalization, C_{60} is expected to be an efficient nonlinear optical material. A large nonlinear third-order susceptibility of a C_{60}-benzene solution has been reported.[4] Although a second-order nonlinear response of C_{60} has also been reported it was too weak to analyze.[5]

In this letter, we report new measurements of the second- and third-harmonic generation (SHG and THG) in C_{60} films. We also measured the temperature dependence of the second-order nonlinear susceptibility in a corona poling electric field of 6 kV, as well as the film thickness dependence of the second harmonic intensity. We speculate on the origin of the large SHG from C_{60} films, given that the isolated molecule itself has inversion symmetry.

C_{60} powder was prepared by contact-arc evaporation of graphite in a He environment.[6] The soluble components of the resulting soot were extracted with toluene and separated (from other fullerenes) by column chromatography.[7] The purity was examined by Raman, IR absorption, high-performance liquid chromatography, and fast atom bombardment mass spectroscopy and was better than 99%. C_{60} thin films, with thicknesses between 100 Å ~ 2 μm, were deposited on glass substrates by thermal sublimation at 350–400 °C under an ambient chamber pressure of 1.5×10^{-7} Torr. The as-deposited films are smooth, shiny, and yellow in color.

We measured the reflection SHG using the equipment and techniques described elsewhere.[8] Figure 1 shows the *p*-polarized SHG intensity when pumped by an *s*-polarized beam as a function of the rotation angle about the film normal. We note that the intensity is the same in all directions. Measurements for other polarization combinations yield the same results. The film is therefore isotropic about its normal. A uniaxially symmetric film may be represented by two $\chi^{(2)}$ components. (This assumes Kleinmans symmetry which is a good approximation when no resonances are involved.) By measuring the *p*-polarized SHG for various polarizations of the fundamental wave, we can determine the ratio of these two components. Figure 2 shows the *p*-polarized SHG intensity as a function of the polarization angle (which is measured relative to the incident plane). By fitting this data to the appropriate expressions we obtain the ratio $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz} = 0.46$

The transmission SHG measurements were carried out at 1.064 μm in the *p*-polarized geometry using instrumentation and calibration techniques described previously

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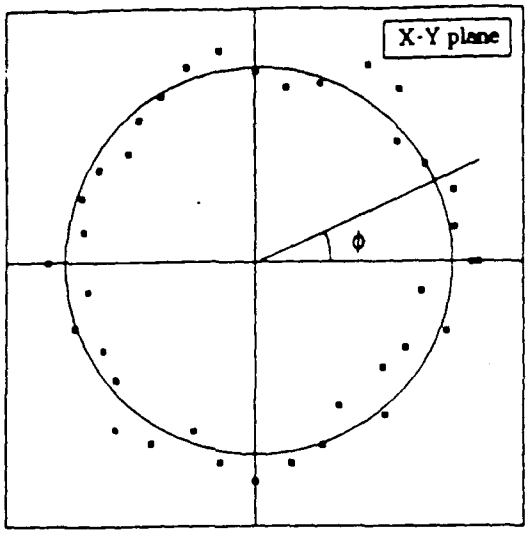

FIG. 1. *p*-polarized, reflection-SHG intensity when pumped by an *s*-polarized beam as a function of the rotation angle about the film normal.

The SHG intensity for different incident angles is shown in Figure 3. Again fitting the data to the appropriate theoretical expression, we determine the ratio of the components as: $\chi^{(2)}_{z,yy}/\chi^{(2)}_{z,zz} = 0.48$, which is consistent with the value obtained from the reflection SHG measurements. Since we do not observe Maker fringes in these measurements the film thickness must be much smaller than the coherence length. SHG was studied on films with different thicknesses (the film thickness was measured using a Tencor Alpha-Step film profiler). Figure 4 shows that the square root of SHG intensity increases linearly with the film thickness. Clearly the C_{60} film shows a bulk second order nonlinearity. The intercept in Fig. 4 corresponds to the surface SHG contribution.

The values of $\chi^{(2)}$ for the film were determined by comparison with the bulk $\chi^{(2)}_{z,zz}$ contribution to the transmission SHG of a quartz plate measured under the same conditions (using the formalism of Jerphagnon and Kurtz

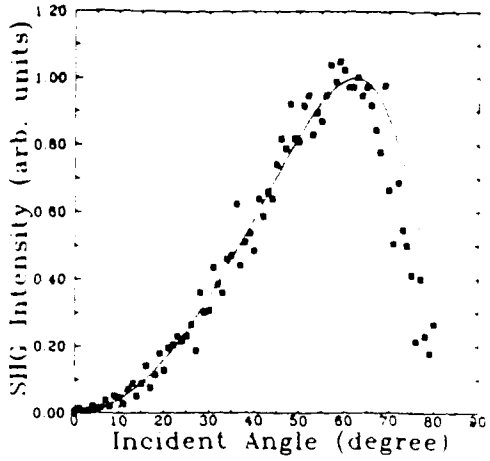

FIG. 3. Transmission-SHG intensity from a film as a function of the fundamental beam incident angle. The solid line is a theoretical curve generated for $\chi_{z,yy}/\chi_{z,zz} = 0.48$.

for uniaxial materials and the $\chi^{(2)}$ component ratio obtained from our films).[10] We obtain $\chi^{(2)}_{z,zz} = 2.1 \times 10^{-9}$ esu for our C_{60} films. This value is about 1.5 times that of quartz. The SHG signal decreases slowly with time when the film is exposed to air.

Corona film poling was carried out using techniques described earlier.[9] The film was held at a +6 kV potential and the transmission SHG was recorded while heating the film from room temperature to 170 °C. The SHG intensity starts to rise at a temperature of 90 °C, reaches a maximum at 140 °C and then falls with increasing temperature. The SHG follows the same route when cooling, except that the maximum value is reduced, as shown in Fig. 5. We believe this reduction is due to thermal damage and/or film evaporation. We do not observe a significant reduction if we start the cooling at a temperature below 140 °C. The maximum observed value of $\chi^{(2)}$ is about 2×10^{-8} esu, which is about 10 times larger than its value at room temperature. After cooling, the film still shows a SHG enhancement behavior when it is reheated. We do not see the enhance-

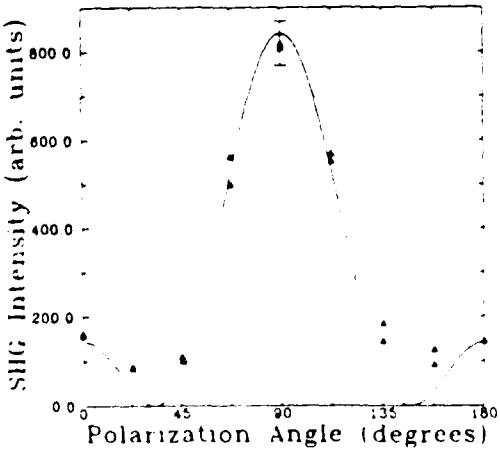

FIG. 2. *p*-polarized, reflection-SHG intensity as a function of the polarization angle relative to the input fundamental beam. The solid line is the theoretical curve for $\chi_{z,yy}/\chi_{z,zz} = 0.46$.

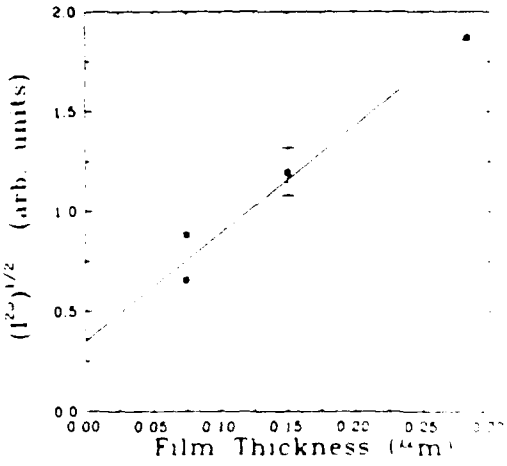

FIG. 4. Square root of the second harmonic generation intensity as a function of the film thickness.

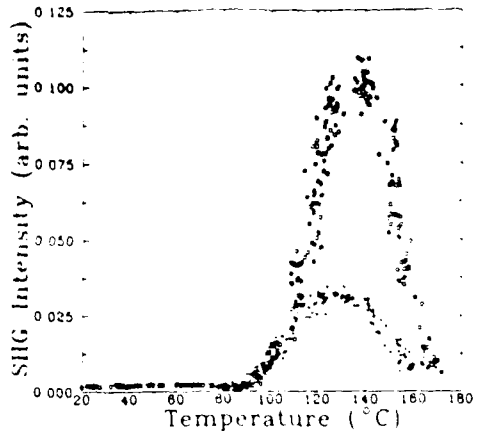

FIG. 5. SHG intensity from a film under poling potential of +6 kV as the temperature is swept

ment while poling at room temperature. At the same time we do not observe the enhancement at a nominal temperature of 140 °C without the application of the high voltage.

We now discuss some potential mechanisms for SHG. At room temperature the C_{60} crystal structure has central symmetry.[3] It is possible that in the bulk sample, small amounts of impurities with noncentral symmetry may be present (e.g., C_{60} isomers, other higher fullerenes, or oxides such as $C_{60}O$). Substrate induced orientation (and poling) would then be invoked to account for a macroscopic room-temperature polarization. Energy dispersive x-ray measurements show no evidence for heavier elements. However, Auger spectroscopy measurements on samples transferred through air show the presence of an oxygen line, comparable in intensity to carbon. Assuming the SHG activity is associated with impurities, it is then apparent that systematic studies of large fullerenes as well as chemically derivatized C_{60} molecules and accompanying SHG characterization should be undertaken. Given that the present impurity population is not large, this explanation would predict that considerably larger enhancements are possible.

A second possibility is that the SHG is caused by electric quadrupole (or magnetic dipole) contributions which are allowed in centrosymmetric materials (the electric dipole contribution is forbidden). The electric quadrupole and magnetic dipole contributions are generally smaller by a factor $ka(\sim 10^{-3})$ than the electric dipole contributions, where k is light wavevector ($\sim 10^{4}$ cm^{-1}) and (in our case) a would be of order the molecule diameter (about 7×10^{-8} cm). However, the effective number of electrons participating in the formation of the dynamic quadrupole greatly exceeds one

One could conjecture that the origin of the temperature/field-induced electric dipole might involve oxidation or degradation of the molecular structure of C_{60} due to exposure to the atmosphere and a corona discharge at elevated temperature. To address this latter possibility, films with a 2000 Å overlayer of evaporated SiO_2 were prepared (to suppress interaction with the environment). These "protected" films do show better performance than the noncoated films in all respects (e.g., negligible decrease of the SHG when the film is exposed to air and greatly improved retention of the poling-field-enhanced SHG upon temperature recycling).

Experiments were performed in which the poling field was removed. Within our time resolution (~ 0.1 s, governed by the pulse repetition rate) the enhanced laser SHG effect disappeared in 0.4 s. This suggests the observed effect does not arise from poling in the usual sense (where existing static dipoles are oriented by slow activation process under the influences of the field).

Initial measurements of third harmonic generation from our C_{60} films were performed at 1.907 μm by Raman shifting of the 1.064 μm pulse from a Nd:YAG laser. The measured $\chi^{(3)}$ value is $\sim 2\times 10^{-11}$ esu.

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